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SUSTAINABLE PRODUCTION OF GRAPHENE FROM PETROLEUM COKE

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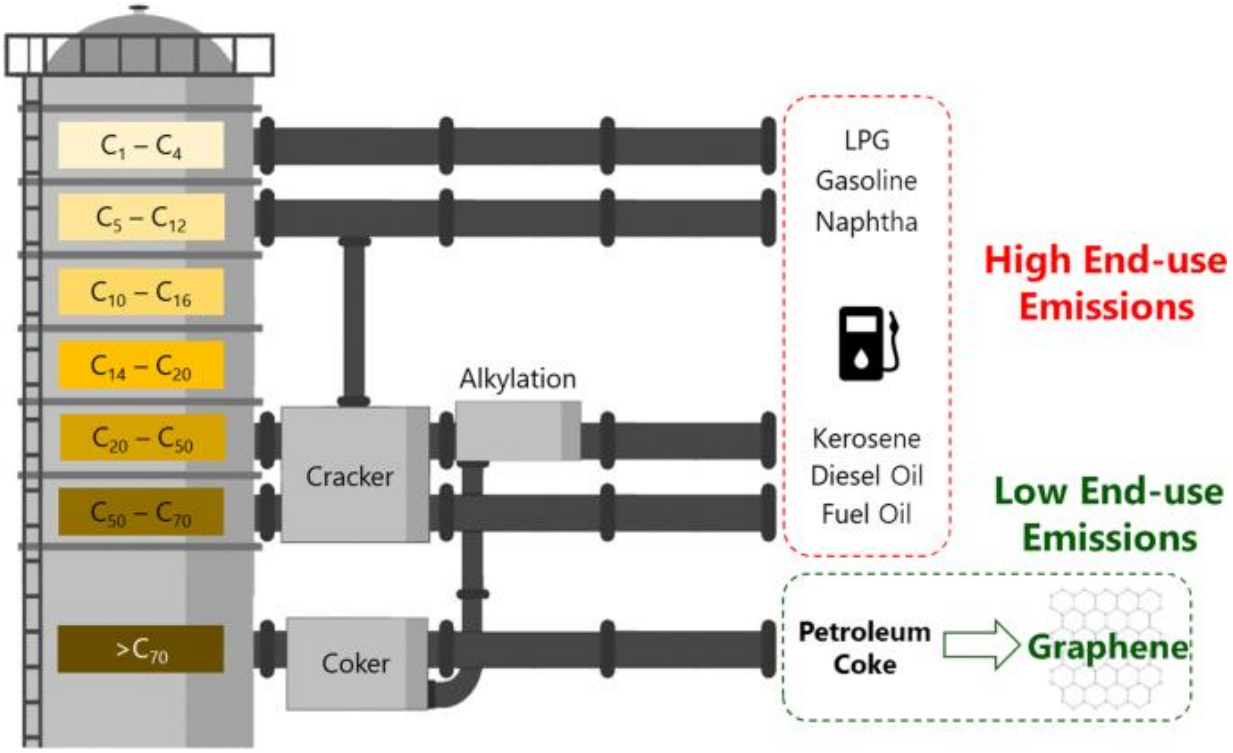
Abstract

The objective of the present work was to synthesize a graphene-like structure from petroleum coke (pet coke). Graphene is a potential alternative conducting material to replace traditional electrode materials such as indium tin oxide. The phosphoric acid was used to activate the pet coke in conditions where the coke to acid ratio is varied as 1:1, 1:2, 1:3, 1:4 and 1:5. The samples were kept at different temperatures in the furnace maintained in inert atmospheric conditions at 400, 500 and 600 °C for activation time intervals of 1, 2 and 3 h. The extent of activation of pet coke samples was characterized by their yield and iodine number. For the optimized conditions (600 °C, 3 h, 1:4 coke to acid ratio), the activated pet coke was moulded and taken as the anode for electrochemical exfoliation using platinum wire as cathode, and 0.3 M H2SO4 solution as electrolyte. The electrochemical exfoliation was carried out using DC power supply at 22 V for 8 h, and the obtained exfoliated product was analysed by surface-sensitive techniques (XRD, Raman and SEM). The specific capacitance values were measured using cyclic voltammetry in KOH, Na2SO4 and H2SO4 electrolytes. The highest specific capacitance value of 40 F g-1for the scanning rate of 25 mV s-1 was obtained in 1 M H2SO4. It was confirmed that graphene-like structure produced from activated pet coke can be used as an alternate material for supercapacitor applications.

Introduction

With the continuing rise in concern over sustainable resource use, the petrochemical industry faces challenges in managing each of its product streams. Even by-products of oil refining, such as petroleum coke, are difficult to utilize sustainably; coke is produced by heating resids or slurry oils from refinery units such as Fluid Catalytic Crackers. Coke is used as a fuel for heating in several industries, and the combustion of coke produces more CO_2 per fuel mass than coal1. Coke is also used in the steel and aluminum industries as an anode for smelting, a process that also emits greenhouse gases2. These concerns highlight the global need to repurpose existing petroleum streams such as coke and its precursor oils toward sustainable end-uses (Fig. 1).

Fig. 1: Schematic of Refinery Products.



Simplified schematic of refinery operations and products: there is a need to push these petroleum streams toward products with low end-use emissions, such as carbon nanomaterials.

Here, we demonstrate the use of petroleum coke as a feedstock for carbon nanomaterial production. Graphene, in particular, is an exciting target because of its ongoing deployment into a range of application fields including batteries, supercapacitors, structural materials, transparent electronics, and flexible wearable devices3,4. It is highly desirable to expand the suite of graphene precursors to include existing industrial by-products.

The economics of possible coke-to-graphene processes are quite striking: needle coke, the highest quality grade of petroleum coke, can be used for electrodes in steel production and can be purchased for ~$1500–3000/ton.

Bulk graphene powder can be purchased at the lab scale for as little as ~$8/gram, orders of magnitude more valuable than coke. This latter price will decrease with scaleup, but this is still an order-of-magnitude increase in economic value.

In addition, petroleum coke provides an additional feedstock for graphene production. Natural graphite is a finite source; it is estimated that 800 million tons can be recovered worldwide[5]. Furthermore, much of it is difficult to use or unusable for graphene production because only 10–15% of natural graphite is actually graphitic carbon; most of it is amorphous and contains silicate minerals or metals[5]. In contrast, needle coke can be consistently produced with high graphitic content and low impurity concentrations. Global needle coke production was at 1.1 million tons per year as of 2020, and it is expected to increase to 1.5 million tons per year by 2026[6]. However, these numbers are based on the demand for needle coke for the steel and lithium-ion battery industries; needle coke production can be significantly increased to meet additional demand if needed. Although petroleum (and therefore petroleum coke) is also a finite resource, progress has been made toward producing needle coke from renewable feedstocks such as biomass[7] or plastic waste[8]. Not only can needle coke be a more permanent feedstock for graphene production, but this avenue also the petroleum portfolio away from high-emission end-uses.

Graphite-derived graphene is well-documented[9,10,11], but coke-derived graphene has not been extensively explored. Prior work on the production of graphene from coke has largely focused on graphene oxide (GO) and explored the effect of crystallinity on the resulting lateral size[10,12,13]. Ball-milling coke with stearic acid has also been explored[14], but questions remain about the distinction between the parent material and the final graphene-like product, particularly in their Raman signature. This is likely related to a lack of effective separation procedures in place.

Our group recently demonstrated the potential for high-yield and scalable production of high-quality graphene nanosheets using an electrochemical exfoliation (ECE) method in a compressed expandable chamber[15,16]. The compressed reactor allows for expansion of the parent material as it is exfoliated while maintaining electrical contact throughout the mixture. (This is superior to conventional electrochemical methods that use graphite monoliths as a parent material; the exfoliation process breaks apart the graphite monolith, losing electrical contact and halting the reaction.) The resulting nanosheets are termed electrochemically exfoliated graphene (EEG). Simpler ECE procedures have been attempted on coke before, but the resulting material either formed small graphene quantum dots or required additional post-processing exfoliation[17,18].

Supercapacitor is an electrochemical energy storage device that attracts a lot of attention due to its higher power density, fast charge and discharge rate, and good stability.

Generally, porous forms of carbon materials have been used in supercapacitors as energy storage media because of their large surface area, favourable pore size distribution, high conductivity and chemical stability. To prepare activated carbon material, various carbon-rich raw materials can be used, such as rice husk, bamboo, banana fibres, sugar cane bagasse, cassava peel waste, etc. Pet coke can also be used as a precursor for carbon and conversion to a graphene-like structure. Many authors studied and activated the petroleum coke with different activation techniques. The activated coke is converted to a graphene-like structure. Graphene has a two-dimensional honeycomb sp2 carbon lattice and exists in different forms, such as graphene oxide (GO) and reduced graphene oxides (RGO). These materials have many potential applications in the future, while currently, they are mostly used for biomedical applications and energy storage devices due to their excellent electrical, mechanical and chemical properties.

In this work, different needle coke grades are evaluated as the parent material for the ECE process in a compressed chamber. The reactor product contained unreacted material, unwanted small particles, and a graphene-like product, termed Coke-EEG, which was isolated by a two-step centrifugation method. The morphology and composition of the final product confirm that this material is indeed a graphene-family material. This finding is at the core of a new industrial push toward the use of natural gas and petroleum streams to produce high-value nanomaterials

Experimental

Petroleum coke

Petroleum coke was collected from the Turkmenbashi oil refinery plant, which is a carbon residue left after distillation of petroleum. All the chemicals, such as phosphoric acid and sulfuric acid, and used for experiments without further purification. Moisture, ash, volatile matter and fixed carbon contents of the pet coke were analyzed by typical proximate analysis techniques icles are sieved in the sieve shaker. An average particle size was measured as 150 □m.

Chemical activation of petroleum coke

The petroleum coke sample of 3 g was activated by chemical activation using phosphoric acid. Pet coke and phosphoric acid were mixed in the ratio of 1:1 (1 g of coke and 1 g of 90 % H_3PO_4) 1:2, 1:3, 1:4, and 1:5, kept in the furnace and maintained in inert atmospheric condition at a temperature of 400, 500 and 600°C, respectively, during time intervals of 1, 2 and 3 h. The samples were allowed to cool to room temperature, washed repeatedly with distilled water to remove the excess of present chemicals, and dried in a hot air oven at 105 °C at a time interval of 2 h. The activation of petroleum coke was analyzed by yield percentage and iodine number.

The iodine number is measured using the standard procedure. 10 ml of 0.05 M iodine solution was taken in a conical flask, and two drops of 1 % starch solution were added. The pale yellow colour of the iodine solution turns blue. The solution was titrated with 25 mM sodium thiosulphate till it became colorless. Burette reading that corresponds to blank reading was noted as (B). Then 0.2 g of activated coke was taken in the iodine flask and 40 ml of 0.05 M iodine solution was added. The solution was shaken for 4 minutes prior to filtering. 10 ml of the filtrate was titrated against thiosulphate solution using starch as an indicator and the titrated value is noted as (A). The iodine number (mg g-1) was determined by equation (2), and the activated pet coke was dried and stored in a desiccator.

Electrochemical exfoliation

Electrochemical exfoliation was performed in an electrolysis cell. The typical experimental setup and its lab photo are shown in Figure 1. The synthesized graphene is mixed with polyvinylidene fluoride (PVDF) as a binder at the weight ratio of 9:1, the weight ratio of 18 g of activated pet coke and 2 g of PVDF binder. The mixture was moulded in a mechanical press at 100 °C and 100×105 N m-2 pressure. A sample of 10 cm in length and 15 mm in diameter of formed solid coke was taken as an anode and Pt wire as a cathode. The coke was connected with a wire and attached to the DC power supply, while the wire contact with the solution was protected by glue to avoid the connected wire dissolution during the reaction. This whole anode assembly was dipped into 0.3 M H_2SO_4 solution to immerse coke in the electrolyte fully. The electrochemical exfoliation was carried out by applying DC voltage ranging from 12 to 28 V for 8 h. The sample weight of 10 g per run was taken. After exfoliation, the sample was allowed to settle down in the cell and then the sample was filtered. The filtered samples were dried in a hot air oven at 80 °C for 1 hour and then analyzed.

Results and discussion

Activated petroleum coke

Activated petroleum coke yield and iodine number were experimentally determined for different activation temperatures (t): 400, 500 and 600 °C, different coke to phosphoric acid weight ratios: 1:1, 1:2, 1:3, 1:4, 1:5 and different activation times: 1, 2 and 3 h.

The iodine number is an important parameter for energy storage applications because it provides insight into the materials' surface area, porosity, and ability to adsorb and desorb molecules. The iodine number is a measure of the microporosity and surface area of the activated carbon. Activated pet coke with high iodine number typically has a large surface area and micropores. High surface area and porosity can enhance the material's capacity to adsorb and store ions, an important supercapacitor property. Data in Table 2 show that the iodine number of activated petroleum coke increases with an increase in temperature, coke-to-phosphoric acid ratio and activation time. The iodine number of activated petroleum coke prepared with an activation temperature of 600 °C is higher than 400 and 500 °C for all ratios.

This is due to more extensive volatile matter degradation at higher activation temperatures. For temperatures beyond 600 °C, there is no improvement in the activation property observed. The highest iodine number is obtained after 3 h of coke activation at the activation temperature of 600 °C and coke-to-acid ratio of 1:4, and just this particular sample of activated coke was used for further examinations.

Conclusions

In this investigation, petroleum coke was activated using phosphoric acid and the activated pet coke was subjected to electrochemical exfoliation in an H2SO4 solution to produce a graphene-like structure material. Operating parameters for the activation of coke (pet coke to H3PO4 ratio, temperature and time of activation) and electrochemical exfoliation (voltage, concentration of H2SO4 electrolyte and time of exfoliation) were studied, defining the best-activated pet coke sample and the highest yield of exfoliated graphene. The exfoliated graphene material was tested for supercapacitor application in Na2SO4, KOH and H2SO4 electrolyte solutions, showing the highest specific capacitance of 40 F g-1 at 25 mV s-1for the graphene/1 M H2SO4 system. It is concluded that graphene-like structure material derived from the exfoliation of activated pet coke can be used as supercapacitor material for electrochemical energy storage applications.

References

[1] Y. Shan, D. Guan, J. Meng, Z. Liu, H. Schroeder, J. Liu, Z. Mi, Rapid growth of petroleum coke consumption and its related emissions in China, Applied Energy 226 (2018) 494-502. https://doi.org/10.1016/j.apenergy.2018.06.019

[2] R. Aravind Raj, V. Manimozhi, R. Saravanathamizhan, Adsorption studies on removal of Congo red dye from aqueous solution using petroleum coke, Petroleum Science and Technology 37 (2019) 913-924. https://doi.org/10.1080/10916466.2019.1575866

[3] R. Priyadharshini, R. Saravanathamizhan, V. Manimozhi, J. Manokaran, N. Balasubramanian, Preparation of activated petroleum coke for supercapacitor application, Energy Storage 2 (2020) e151. https://doi.org/10.1002/est2.151